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## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Process for the Production of High Molecular Weight Polyamides

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the production of melts of high molecular weight polyamides with especially high stability.

High molecular weight linear polyamides, such as poly-ε-caprolactam and polyhexamethylene-adipamide, are suitable for a large number of technical purposes because of the outstanding chemical resistance and the excellent mechanical properties of moulded articles produced therefrom. If these poly-articles are moulded *via* the melt, then they form melts of extraordinary low viscosity and are, because of the low melt state occasioned thereby, scarcely suitable for the production of profiles, pipes, deep drawn parts and, especially, blown articles.

It has already been suggested to increase the viscosity of the polyamide melts by the addition of cross-linking agents which are able to react with the reactive hydrogen atoms. As cross-linking agents there can be used for this purpose, for example, epoxy resins and epoxy group-containing lower molecular weight compounds, as well as isocyanates. Examples of compounds of this type include di- or polyepoxides of mono- or polybasic amines, such as N-di-(2,3-epoxypropyl)-aniline, hexamethylene-diisocyanate or agents splitting off isocyanates, such as the adduct from 2 mol of phenol or 2 mol of ε-caprolactam and one mol of hexamethylene diisocyanate.

Good results are also obtained with di-

epoxides of dicyclohexenyl-alkanes in amounts of about 0.5 to about 1.5 percent by weight in the case of polyamides of the usual molecular weight, i.e. with molecular weights of about 20,000—30,000, corresponding to a relative viscosity of about 2.3 to about 2.6 in a 1% solution in *m*-cresol at 25°C. The more epoxides are added to these polyamides, the higher becomes the viscosity of the melts. In this manner, there can be produced useful polyamides with a relative viscosity of up to about 4.0. Although polyamides of this type can very readily be worked up in the usual worm extruders, their melts are still not sufficiently stable, especially for the production of blown articles and certain semi-finished articles. A further increase of viscosity and stability by the addition of larger amounts of epoxides, for example, 2 percent by weight, does not give the desired result because the melts then become rubber-elastic. As a result of the high resiliency of such melts, difficulties of conveying occur in the extruder which lead to an uneven output and inexact measuring and thus to inferior formed articles.

It is also known to produce polyamides with increased molecular weight, for example, of more than 30,000, corresponding to a relative viscosity of more than about 4.0, by polymerisation in the melt or by post-condensation in the solid state, said polyamides exhibiting a higher melt viscosity and an improved molten state. However, these products are also of only limited suitability for the production of profiles, pipes, blown articles and deep drawn parts. In the blow moulding process, only hollow articles with a capacity of up to about 2 litres can be obtained reasonably satisfactorily. However, in the case of blown articles of this size, the still insufficient molten state of these products already becomes clearly noticeable. The

blown articles do not have a uniform wall thickness and tend to become distorted. Larger containers cannot be manufactured at all. Sheets produced from this material have, upon heating, a strong tendency to sag and are, therefore, not suitable for the deep drawing process. Rods can be reasonably satisfactorily produced from this material only in diameters of more than about 20 mm.

- 10 We have now found that high molecular weight cross-linked polyamides with a high melt viscosity and an especially high molten state which are outstandingly suitable for the production of profile parts, pipes, deep drawn parts and blown articles, can be obtained by a process which comprises reacting a synthetic linear thermoplastic polyamide having a molecular weight of at least 40,000 with 0.1 to about 2% by weight of a cross-linking agent.

- 20 In contradistinction to the known cross-linked melts produced from polyamides of low molecular weight, the polyamide melts produced according to the present invention offer no conveying difficulties in the extruder but emerge uniformly and smoothly from the extruder and can, therefore, be measured satisfactorily. Since, in spite of their high stability, they surprisingly exhibit no rubber-elastic behaviour, they can also be moulded, without difficulty, into large articles. Thus, for examples, a melt tube of high stability is obtained by extrusion which can be inflated in a suitable mould, without difficulty, and can be moulded into hollow articles of uniform wall thickness which no longer tend to distort. It is, for example, possible to produce hollow articles, such as flasks, fuel tanks and containers of all kinds, with a capacity of up to about 60 litres, by the blowing process. Furthermore, the material can be worked up, without difficulty, to sheets of, for examples, 1mm. thickness which can be satisfactorily moulded by deep drawing to form moulded articles with good lateral rigidity. Bubble-free rods with diameters of, for example, 10 mm., can also be satisfactorily produced by extrusion.

- 50 Polyamides in the meaning of the present invention are all the synthetic, thermoplastic polyamides known in the art, such as the polymerization products of lactams with at least six ring members for example of  $\epsilon$ -valerolactam,  $\epsilon$ -caprolactam and  $\omega$ -octanethiolactam, the polycondensation products of the corresponding  $\omega$ -amino-carboxylic acids, as well as of diamines and dicarboxylic acids, such as tetra-, penta- and hexamethylenediamines, and succinic, glutaric, adipic, pimelic, azelaic and sebacic acids, and mixed polyamides.

- 60 As cross-linking agents suitable for carrying out the process of the present invention, there may be used all the compounds which are known in the art for this purpose, the

most important of which are mentioned above. In addition, there may be mentioned high molecular weight meltable polycarbonates, especially those of aromatic dihydroxy compounds, preferably bis-phenols, such as bis-(hydroxyphenyl)-alkanes and cyclo-alkanes.

The amounts of the mentioned cross-linking agents expediently to be added to the melts can vary within wide limits and depend essentially on the nature of the polyamide used and on the properties of the end products to be achieved. They can be readily determined from case to case by simple experiments. In general, additions of about 0.1 to about 2 percent by weight suffice. In complete contradistinction to the polyamides of normal molecular weight, larger amounts, as a rule, no longer significantly increase the melt viscosity of the polyamides.

The cross-linking agents are preferably mixed with the polyamides in the usual manner for example, by addition thereto after their production. It is especially advantageous intimately to mix polyamide granulates with the cross-linking agents and then to melt them continuously and briefly, for example, according to the process of Patent Specification No. 820,823.

Apart from cross-linking agents, other materials can also be added to the linear polymers in order to modify their properties. There may be mentioned, for example, antiageing agents, pigments, dyestuffs, metal powders, fillers, plasticisers, resins and other synthetic and natural materials, crystallisation nuclei and mould-release agents.

The following Examples are given for the purpose of illustrating the present invention:—

#### EXAMPLE 1.

20 kg. of granulate of a polyamide 6 of molecular weight 50,000 are mixed for two hours in a spin roller with 120 g. di-(3,4-epoxy - cyclohexenyl) - dimethyl - methane and homogenised *via* an extruder with a simple three-zone worm, drawn off as bristle, chopped up and dried.

(a) If the granulate obtained is melted in an extruder and extruded through an annular nozzle, then a melt tube is obtained which is placed in a blow mould and moulded with pressurised air to give a container of 20 litres capacity.

(b) Sheets of 0.5—3 mm thickness, produced from the above granulate in an extruder with a slot nozzle, are cut into pieces of suitable size, softened with hot air in a deep drawing apparatus and, after placing on a plug, moulded by vacuum to form a cylindrical container.

(c) From the granulate, melted in an extruder and extruded, with cooling, through a suitable nozzle into a calibration device, there are obtained, without difficulty bubble-

free rods of less than 10 mm. diameter by the usual continuous and discontinuous production processes.

#### EXAMPLE 2.

- 5 As stated in Example 1, 20 kg. of pure granulate from polyamide 6 of molecular weight 50,000 are mixed for two hours in a spin roller with 120 g. di-(3,4-epoxy-cyclohexenyl)-dimethyl-methane. This granulate is
- 10 subsequently melted *via* an extruder and extruded through an annular nozzle. As in Example 1, there is obtained a melt tube which can be moulded in the manner there described to a container of 20 litres capacity.
- 15 Similar results are obtained when proceeding in the manner described in Example 1 but with the difference that there is used 1% by weight, referred to the polyamide, of the adduct of 1 mol of hexamethylene diisocyanate and 2 mol of  $\epsilon$ -caprolactam or 0.7%
- 20 by weight of a powdered polycarbonate of bis-phenol A (relative viscosity 1.3 in 1% *m*-cresol solution at 25°C.) instead of 0.6% by weight of di-(3,4-epoxy-cyclohexenyl)-dimethyl-methane.
- 25

#### WHAT WE CLAIM IS:—

1. Process for the production of high molecular weight cross-linked thermoplastic polyamides having a high melt viscosity, which
- 30 comprises reacting a synthetic linear thermoplastic polyamide having a molecular weight of at least 40,000 with 0.1 to about 2% by weight of a cross-linking agent.
2. Process according to claim 1, wherein

the polyamides have a molecular weight of 50,000 to 60,000. 35

3. Process according to any of the preceding claims, wherein there is also added at least one antiageing agent, pigment, dyestuff, metal powder, filler, plasticiser, resin, synthetic material, natural material, crystallisation nuclei material and/or mould-release agent. 40

4. Process according to claim 1 for the production of melts of high molecular weight polyamides, substantially as hereinbefore described and exemplified. 45

5. High molecular weight polyamides of high melt stability, whenever produced by the process according to any of claims 1 to 4. 50

6. Polyamides of high melt stability with a molecular weight of at least about 40,000 cross-linked by about 0.1 to about 2% by weight of a cross-linking agent. 55

7. Shaped bodies, whenever prepared from polyamides according to claim 5 or 6.

8. Thin-walled containers, whenever produced from a high molecular weight polyamide according to claim 5 or 6. 60

9. Thin-walled containers according to claim 8, with a capacity of at least about 20 litres.

10. Fuel tanks, whenever produced from a polyamide according to claim 5 or 6. 65

For the Applicants,

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